THE INTERACTIONS OF CONTAMINATION PRODUCTS WITH THE SPACE ENVIRONMENT: *IN-SITU* ELECTRON SPECTROSCOPY STUDIES OF UV-IRRADIATED SILICONES

A FINAL REPORT

SUBMITTED BY

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SUBMITTED TO THE U.S. AIR FORCE

JUNE 2001

20010806 108

AQ FOI-11-2183

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 13-July-2001	3. REPORT TYPE AND DATES COVERED Final Report

4. TITLE AND SUBTITLE

The Interactions Of Contamination Products With The Space Envrionment: In-Situ Electron Spectroscopy Studies Of Uv-Irrdiated Silicones

5. FUNDING NUMBERS

F61775-00-WE074

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

EOARD
PSC 802 BOX 14
FPO 09499-0200

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

SPC 00-4074

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

A

13. ABSTRACT (Maximum 200 words)

This report results from a contract tasking SOREQ Nuclear Research Center as follows: The contractor shall investigate the exposure of spacecraft materials to a simulated low earth orbit environment. The contractor will expose self-prepared silicon polymer samples to a controlled environment of atomic oxygen and UV radiation in their test facility. After each exposure the contractor will use electron spectroscopy to determine the material degradation. The contractor will be paid $5,000 after receipt and acceptance of an initial test plan and the remaining $10,000 after receipt and acceptance of the final report, due 7 months after starting the effort.

14. SUBJECT TERMS

EOARD, Space Environment, space materials, Polymers

15. NUMBER OF PAGES

24

16. PRICE CODE

N/A

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19, SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Abstract

This report summarizes the results of the present research, focused on the effects of simulated Vacuum UV (VUV) irradiation on the outgassing products of silicone-based materials. The black siliconic paint S2, developed by CNES and manufactured by MAP, France, was selected as a contamination source for this work. The outgassing products deposited on Ge substrates were characterized by Fourier Transform Infra Red (FTIR) spectroscopy as consisting predominantly of poly(dimethyl)siloxane.

The outgassing process was studied under different conditions: (i) a standard outgassing procedure according to ASTM E 595 and (ii) a stepwise outgassing at three different temperatures (75°C, 100°C and 125°C). The kinetics of the outgassing process of the S2 black paint at different temperatures was studied using thermoelectric quartz crystal microbalance (TQCM). The composition of the outgassing products collected on Ge substrates was analyzed by X-ray Photoelectron spectroscopy (XPS). The sample containing the high-temperature fraction (125°C) of the outgassing products (collected after evaporation of the other fractions at 75°C and 100°C) was chosen for *in-situ* VUV irradiation.

It was found that the nature and morphology of the outgassing products depends on the outgassing conditions (sample temperature and outgassing rate). The deposited contamination from the 125°C outgassed sample consisted of well-defined droplets, observed by optical microscopy and atomic force microscopy (AFM). After VUV exposure for 25 h (2500 Equivalent Sun Hours (ESH)), the formation of visibly clean regions (free of contamination droplets) was detected in the vicinity of large droplets. This may be an indication of surface migration (or diffusion) of small contamination droplets with subsequent agglomeration into larger aggregates. These large aggregates underwent VUV induced modifications, which resulted in the formation of a specific brain-like texture, monitored by AFM.

The mechanism of the interactions of silicone-based contamination products with VUV irradiation was found to be rather complicated. VUV exposure caused changes in the surface morphology of the deposited samples as well as intra- and inter-molecular rearrangements in the polymeric chains and chemical modifications of the substrate-contamination interface. In addition, a combined QCM and XPS studies showed partial fixation of the contamination layer under VUV irradiation.

The influence of air exposure on the irradiated contaminants was assessed. The obtained results strongly indicated the need and importance of *in-situ* studies of the interaction of the outgassing products with the simulated space environment.

The present work raised new questions and suggested directions for further studies in the field of formation of contamination products and their interactions with the space environment.

1. Introduction

This report describes the results of the present research, focused on the effects of simulated VUV irradiation on the outgassing products of silicone-based materials [1]. For the present work we used the black siliconic paint S2, developed by CNES and manufactured by MAP, France. It is a black matte conductive coating, widely used in optical as well as other space systems. The applied paint is composed of a purified methyl-silicone as a binder, black carbon as pigment and aromatic solvents.

During the past two years, standard outgassing tests (according to ASTM E 595) of different batches of S2 were carried out in our laboratory. Relatively high TML (Total Mass Loss) and CVCM (Collected Volatile Condensable Material) values were obtained in these tests, indicating the potential contamination problems associated with using this paint in the vicinity of optical as well as other surfaces. However, this standard outgassing test should be considered only as a screening process for technological materials, which is unable to answer the fundamental questions involved in the formation of siliconic contaminants and their interactions with the various space environmental elements. These questions should be carefully studied using dedicated simulation and characterization techniques.

The main goal of the present work was to study the nature of the contamination products produced by the outgassing of black siliconic paint S-2 and their interactions with the simulated space environment. Specifically, outgassing under ultra-high vacuum (UHV) conditions and Vacuum VU irradiation of the outgassing products were studied in the present work.

In general, the work was divided into three main stages: preparation of samples, exposure to simulated UV irradiation and characterization of the exposed and unexposed samples by different *in-situ* and *ex-situ* techniques. In order to choose the outgassing conditions, we studied the kinetics of the outgassing process at different temperatures of S2 black paint using thermoelectric quartz crystal microbalance (TQCM). Based on the kinetic results, we decided to study the outgassing products collected on Ge samples under different conditions: (i) stepwise outgassing at three different temperatures (75°C, 100°C and 125°C), and (ii) standard outgassing procedure according to ASTM E 595. The samples prepared by the latter procedure consisted of all fractions of the outgassing products emitted during 24 h at 125°C and collected on a substrate surface at 25°C, whereas the former procedure allowed to collect different fractions separately.

2. Experimental

2.1. Preparation of samples

Black conductive siliconic paint S2 was applied on a pre-cleaned aluminum foil, according to the manufacturer's defined procedure. To study the contamination process, the dry S2 paint was removed as a film from the foil and heated in vacuum up to different temperature levels, depositing the emitted outgassing products at each temperature level on a separate Germanium substrate held at room temperature. The deposition was carried out on polished Ge substrates of 12×10 mm^2 size and 1 mm thickness. The substrates were chemically cleaned with Propanol-2 in an ultrasonic bath for 10 min prior to mounting in the vacuum chamber. The basic pressure in the chamber during the outgassing process was about 1x10^{-7} Torr.

The contaminants were collected at three different temperatures: 75°C, 100°C and 125°C. The same contamination source (3 boats containing 70-90 mg of S2 black paint) was used in this set of experiments. The first three Ge substrates were replaced after 48h of outgassing process at 75°C by a new set of Ge substrates for collecting outgassing products at 100°C. After 24 h at 100°C these substrates were again replaced by a new set for collecting outgassing products emitted during 24h at 125°C. This procedure allowed for the collection of different fractions of the outgassing products, emitted at different temperatures. In another set of experiments, a Ge substrate was used as a collector plate in a standard outgassing test according to ASTM E 595. In this case all fractions of the outgassing products were collected during 24h of heating to 125°C. The batch of S2 black paint used for this work was characterized by the following outgassing properties: TML=0.92%, CVCM=0.11%, and WVR=0.09%.

The outgassing kinetics was determined using our modified ASTM E595 outgassing system, where one collector plate was replaced by a quartz crystal microbalance (QCM). A gold coated 15 MHz sensor, Model MK10 manufactured by QCM research was used. The QCM temperature was controlled by a Peltier element in the –60°C ÷ +100°C temperature range. The exposed area of the QCM was 0.316 cm^2 and its sensitivity was 1.96x10^{-9} gr/cm^2-Hz. An M2000 controller, by the same manufacturer, controlled the QCM heating/cooling rate and sensor temperature. The QCM data and outgassing system parameters were collected by a computer.

2.2. Exposure to simulated UV irradiation

The exposure of selected outgassing products collected on a Ge sample was performed in a unique, compact facility capable of *in-situ* studies of materials exposed to the simulated space environment. The details of the experimental system were described in the submitted proposal [1] as well as in a recent paper [2].

The sample was positioned in the ultra-high vacuum (UHV) system with a base pressure of 1×10^{-10} Torr which incorporated a 30-Watt Deuterium lamp (Hamamatsu Model L-879) producing Vacuum UV radiation of $\lambda = 115-200$ nm. The intensity of the VUV source was calibrated using a phototube sensor (Hamamatsu Model R1187), which could be positioned at the location of the irradiated sample using a linear motion mechanism. The calibration was performed using a 1% filter to reduce the high intensity of the Deuterium lamp to the working range of the sensitive sensor. During the sample's UV exposure the Phototube sensor was shifted to a side position. In the present study the samples were exposed to approximately 100 equivalent sun hours (ESH) during 1h of simulated VUV irradiation (acceleration factor of 100).

The high temperature (125°C) fraction of the outgassing products was exposed to VUV irradiation as a function of time. A continuous data acquisition system was used to control the sample temperature, the intensity of the VUV source and the system's pressure. The intensity of the VUV source was stable during all the exposure periods: 3h, 6h, 12h and 25h. The temperature of the sample holder increased gradually from room temperature to about 50°C after 12 h of a continuous VUV exposure. Concurrently, the residual pressure in the chamber increased up to 1×10^{-8} Torr. At different stages of the experiment (after 6h and 12h exposure time) the irradiated sample was exposed to ambient air for 24h in order to perform *ex-situ* characterization by FTIR and AFM and to assess the difference between *in-situ* and *ex-situ* characterization by XPS.

2.3. Characterization methods

a) In-situ electron spectroscopy measurements

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition and structure of the outgassing products and to measure the changes induced by the VUV irradiation. The XPS spectra were derived using a non-monochromatized Al Kα radiation (1486.5 eV) and a VG Microtech CLAM 2 hemispherical analyzer operating at a pass energy of 100 eV for survey scans and 20 eV for high-resolution scans. An electron "take-off" angle, defined as the angle between the sample surface and the axis of the electron

energy analyzer, was 72°. The binding energy scale was calibrated using the Ag $3d_{5/2}$ line at 368.3 eV as a reference [3]. Elemental composition of surfaces was determined from the high-resolution multiplex spectra using sensitivity factors provided with VG 900w software. Note that XPS is sensitive to the top 30-50Å. This is the typical range of escape depth (inelastic mean free path) of the photoelectrons [4-5].

a) Ex-situ spectroscopic and microscopic analysis

To determine molecular structure the obtained samples were characterized by a Fourier Transform Infrared (FTIR) Spectroscopy. Transmission infrared spectra were recorded using a Nicolet 550 FTIR spectrophotometer. Pristine Ge sample was used for background subtraction. Each spectrum was recorded in a $4000 - 400$ cm^{-1} range using 128 scans at 2 cm^{-1} resolution. Note that transmission FTIR spectroscopy samples the entire thickness of the film and therefore is sensitive to the bulk composition, in contrast to XPS. Selected samples were characterized immediately after the outgassing process, after relatively long storage in air and after exposure to different fluences of VUV radiation.

To study the surface morphology of the outgassing products before and after VUV irradiation, atomic force microscopy (AFM) measurements were carried out using a Digital Instruments Nanoscope II system, operating in the height mode at ambient conditions.

Optical microscopy at low magnification (x160) was used to assess "visual" changes in surface morphology.

3. Results

3.1. Kinetics of the outgassing process

The contaminants' mass deposited on the QCM surface as a function of time is shown in Figure 1. Table 1 summarizes the results of QCM measurements under different conditions. To study the outgassing process at relatively low temperatures, a large amount of S2 black paint was used. For this purpose a specially built large sample boat was filled with ~520 mg of material. It was heated to 50°C for 18h. The mass of deposited outgassing products was as low as $\sim 4 \times 10^{-7}$ gr/cm^2. Then the sample was stepwise heated to 75°C and 100°C for 24h at each temperature. The QCM was kept at 25°C during this time. The mass of deposited outgassing products was $\sim 1.7 \times 10^{-6}$ gr/cm^2 and 3.2×10^{-5} gr/cm^2 at 75°C and 100°C, respectively (see Figure 1(a)). When the sample was heated to 125°C, the mass deposited on the QCM increased rapidly to absolute value of 4.3×10^{-5} gr/cm^2 but after ~2 h a damping of the crystal oscillation was observed (the QCM frequency increased suddenly to "out of the range" values). Note that the full mass sensor range is about 3×10^{-4} gr/cm^2 for the 15 MHz

QCM sensor. However, this range is known to be seriously reduced if the deposit consists of a liquid in a gelatinous state or droplets. An examination by an optical microscope and AFM of the outgassing products collected on a Ge substrate indeed revealed droplets formed by the 125°C fraction of the outgassing products, as it will be described below.

Table 1. Outgassing of the S2 black siliconic paint at different temperatures and re-evaporation of the outgassing products from a gold-coated QCM sensor

Sample temperature °C	QCM temperature °C	Sample mass, mg	Experim. duration, h	Mass deposited on a QCM at the end of experim.		Mass re-emitted from a QCM at the end of experim.	
				gr/cm^2	d*, Å	gr/cm^2	d, Å
50	25	520	18	4.3×10^{-7}	43	-	
75	25	520	23	1.7×10^{-6}	170	-	
100	25	520	24	3.2×10^{-5}	3200	-	
100	25	52	16	5.0×10^{-6}	500	-	
125	25	52	22	5.7×10^{-6}	570	-	
25	25	52	40	-		3.2×10^{-6}	320
25	35	52	22	-		3.9×10^{-6}	390
25	45-50	52	22	-		3.1×10^{-6}	310

Symbol d refers to an average thickness, calculated for a continuous and uniform contamination layer with a density of 1 gr/cm^3, (1 gr/cm$^2 \equiv 1 \times 10^8$ Å)

In order to monitor the outgassing process at 125°C and to study the re-emission of the contamination with increasing QCM temperatures, the initial mass of S2 black paint was reduced by a factor of 10. Figure 1(b) shows the mass deposited on the QCM as a function of time when ~52 mg of S2 black paint was heated to 100°C for 16 h. No significant increase of the QCM mass was found after 16h of heating. The maximum deposited mass of outgassing products at 100°C was 5.0×10^{-6} gr/cm^2. Then the S2 sample was heated to 125°C for 22 h. No damping of crystal oscillation was observed in this case. The QCM was kept at 25°C during all the sample outgassing stage. After that the sample was cooled to room temperature, while the QCM was still at 25°C. At this stage the outgassing process practically stopped while re-evaporation of outgassing products became the dominant process. Re-evaporation kinetics was monitored during 40 h. During this time, the total deposited mass decreased by about 30%. Then the QCM temperature was increased to 35°C, and then to 45°C - 50°C. Thermal emission of the outgassing products was monitored during 22 h at each stage. It was shown that nearly 95% of the outgassing products deposited on the QCM surface could be re-evaporated by heating of the QCM to 50°C.
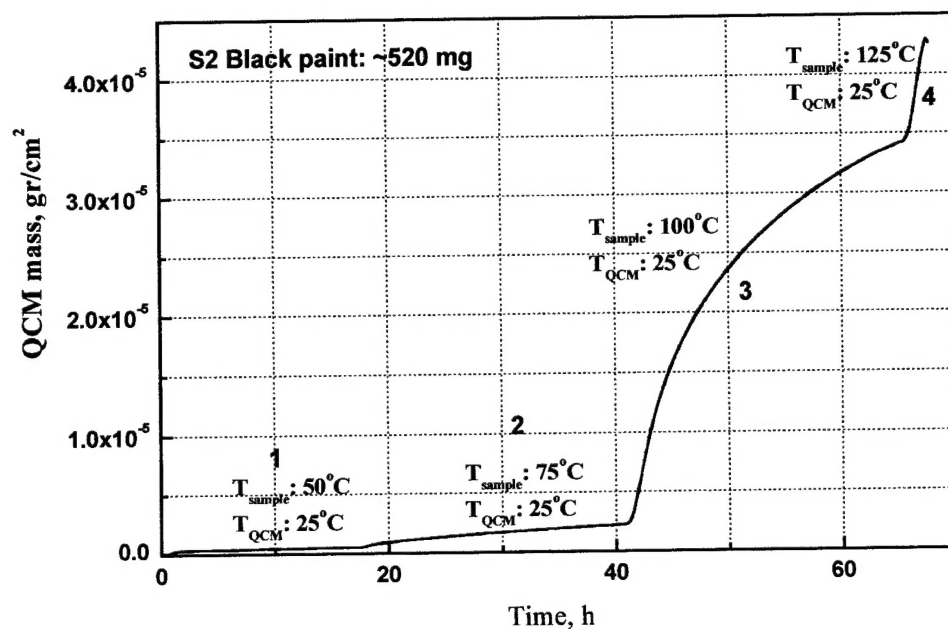
Figure 1(a). The mass of the outgassing products of S2 black paint, collected on a QCM sensor at different sample temperatures. The initial mass of the sample was about 520 mg.
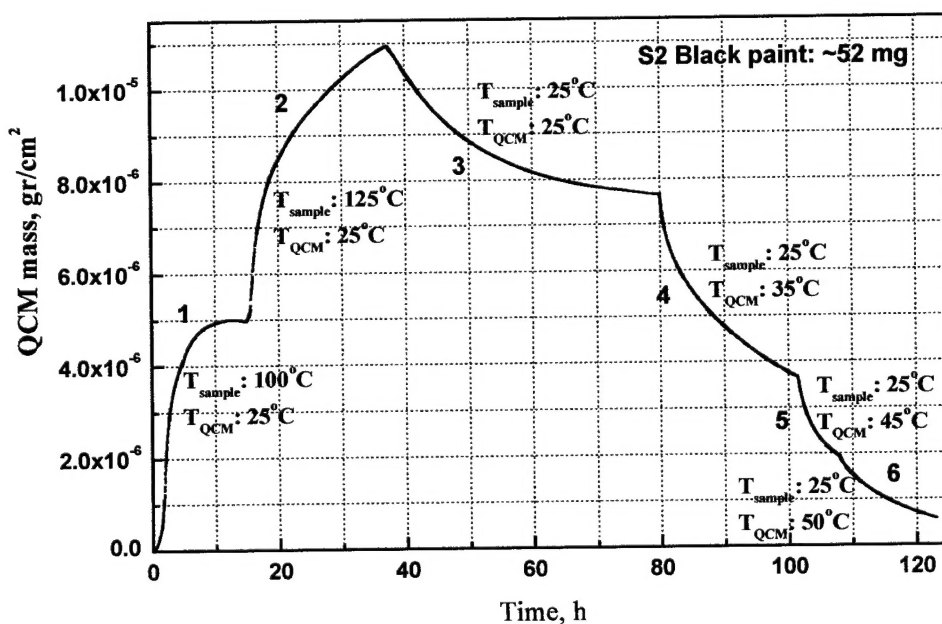

Figure 1(b). The mass of the outgassing products of S2 black paint collected on a QCM sensor at different sample and QCM sensor temperatures. The initial mass of the sample was about 52 mg.

3.2. FTIR studies

The condensable volatile outgassing products collected on Ge substrates were characterized by transmission FTIR spectroscopy. Figure 2 shows FTIR spectra of the contaminated sample analyzed immediately after outgassing at 125°C (high-temperature fraction only) (Figure 2(a)), the same sample after 3 month storage in air (Figure 2(b)) and after 25h of VUV exposure (~ 2500 ESH) (Figure 2(c)).
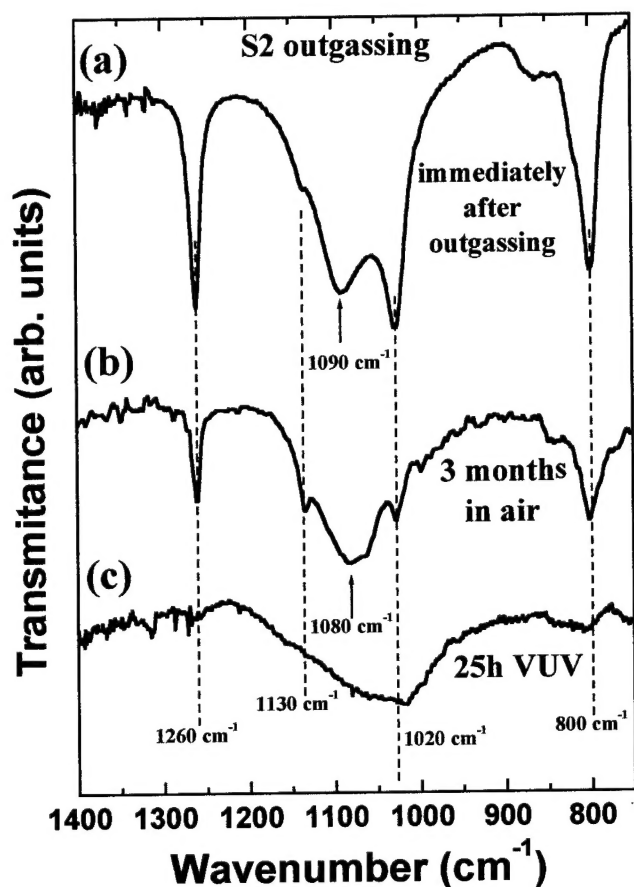

Figure 2. FTIR spectra of the condensable volatile outgassing products collected on a Ge substrate: immediately after outgassing at 125°C (high-temperature fraction only) (a), after 3 months in air (b), and after 25h of VUV exposure (~ 2500 ESH) (c).

The spectrum of the outgassing products immediately after outgassing was similar to that of a siliconic oil composed predominantly of poly(dimethyl)siloxane (PDMS, $[(CH_3)_2SiO]_n$). The most characteristic bands for Si-Methyl group were the $1260(\pm5)$ cm^{-1} band associated with Si-CH$_3$ rocking deformation and Si-(CH$_3$)$_2$ stretching vibration mode

near 800 cm⁻¹. A presence of strong, rather broad doublet pattern at 1020 and 1090 cm⁻¹ reflected open-chain Si-O-Si asymmetrical stretching absorption in siloxane oligomers with a number of coupled units >20 [6-7]. A weak shoulder at 1130 cm⁻¹ indicated the presence of Si-O-C stretching vibrations.

The long storage of the sample in air resulted in some changes in the FTIR spectrum (see Figure 2(b)). First, the increase of transmission intensity indicated partial evaporation of the outgassing products. Then, the intensity of bands in the 1000 – 1100 cm⁻¹ region changed in such a way that a shoulder at 1130 cm⁻¹ became more prominent, whereas the band centered at 1090 cm⁻¹ broadened and shifted toward lower wavenumbers. It is known that the Si-O-Si vibrations in cyclic structures (tetramers and higher rings) give rise to absorption in the 1080-1050 cm⁻¹ range [7]. Broadening of the absorption band may reflect considerable degree of disorder, i.e. variations from average arrangement. Hence, it may be concluded that the storage of the samples in air resulted in some intramolecular transformations in the siliconic outgassing products. However, the bands near 1260 and 800 cm⁻¹ remained unchanged, indicating that no chemical modification of the outgassing products took place.

After 25h of VUV exposure the bands near 1260 and 800 cm⁻¹ almost disappeared. This may indicate breaking of Si-C bonds during VUV exposure. Moreover, the absorption pattern in the 1000 – 1130 cm⁻¹ region was smoothed off. However, its intensity decreased only slightly. The interpretation of these changes is rather difficult and ambiguous. More information about VUV induced changes in the structure of the outgassing products was received from XPS measurements described below.

### 3.3. Morphology of the outgassing products

The condensable volatile products collected on Ge substrates during the outgassing at 125°C (high-temperature fraction only) were characterized by an optical microscope at medium magnification (x160) and by AFM. Figures 3 and 4 show optical micrographs and AFM images (40x40μm), respectively, of a contaminated sample before and after exposure to different fluences of VUV.

The collected outgassing products (125°C-fraction) of the S2 black siliconic paint formed a droplet-type coating on the Ge substrate. Note that no droplets or other well-defined features were observed on the samples on which the low-temperature fractions of outgassing products (emitted at 75°C and 100°C) were collected (images not shown). The optical micrographs showed that the contamination droplets possessed wide size distribution (from a few μm to 20-30 μm in diameter). In addition, a substantial part of the contamination droplets

was located within or in close proximity of microscopic scratches on the substrate surface, possibly formed as a result of a hand-polishing (it is more pronounced on the enlarged original picture). After VUV irradiation for 6 h and then for 12 h and 25 h, part of the droplets possessed more solid-like structure with a specific texture. The size of the modified droplets was much larger than that of liquid ones. It seems that the average size of the modified droplets increased with increasing exposure time. In addition, Figure 3(d) clearly shows that some "clean" region, where no small contamination droplets are detected, surrounds a large modified particle.
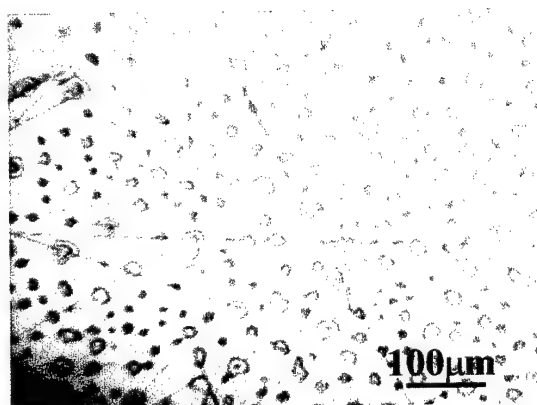
(a) S2 contamination on a Ge surface
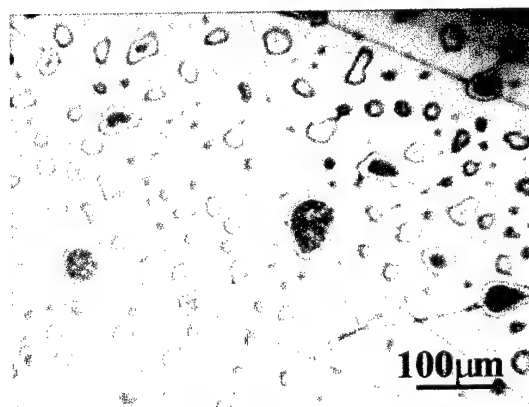
(b) S2 contamination after 6h of VUV
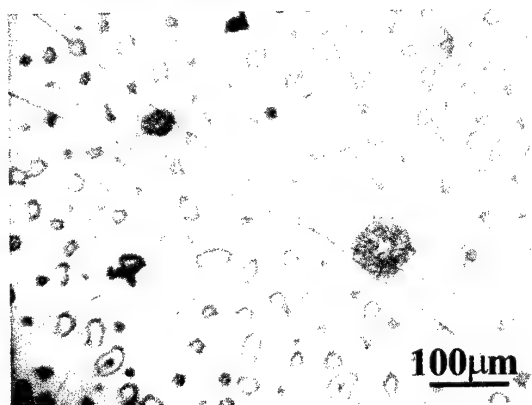
(c) S2 contamination after 12h of VUV

(d) S2 contamination after 25h of VUV

Figure 3. Optical micrographs of a contaminated Ge sample before (a) and after exposure to different fluences of VUV: 6h (600 ESH) (b), 12h (1200 ESH) (c), and 25h (2500 ESH) (d).
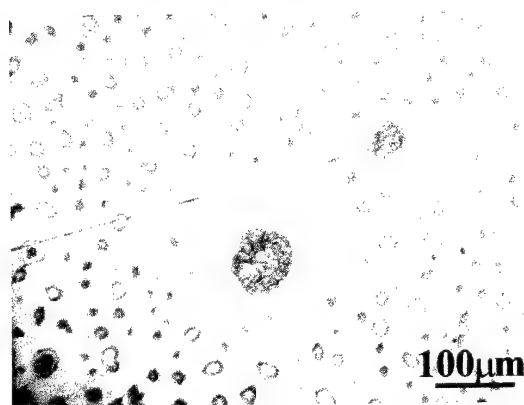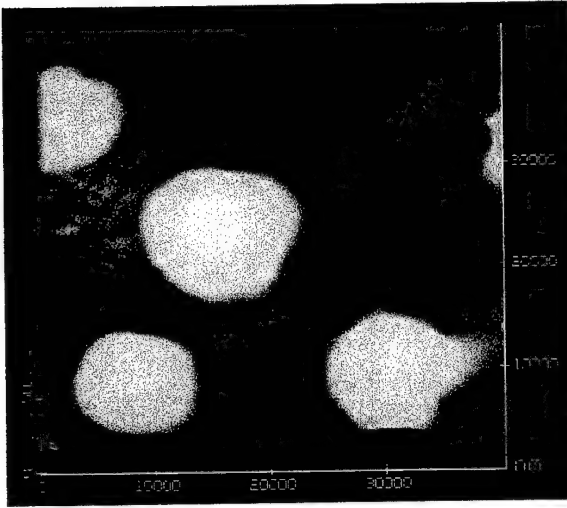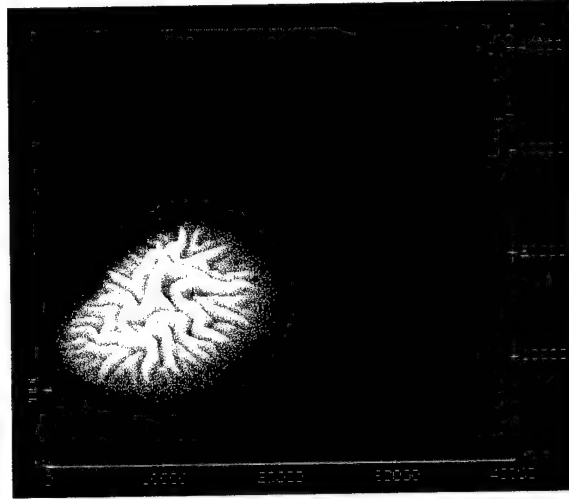
(a) S2 contamination on a Ge surface

(b) S2 contamination after 6h of VUV

(c) S2 contamination after 12h of VUV
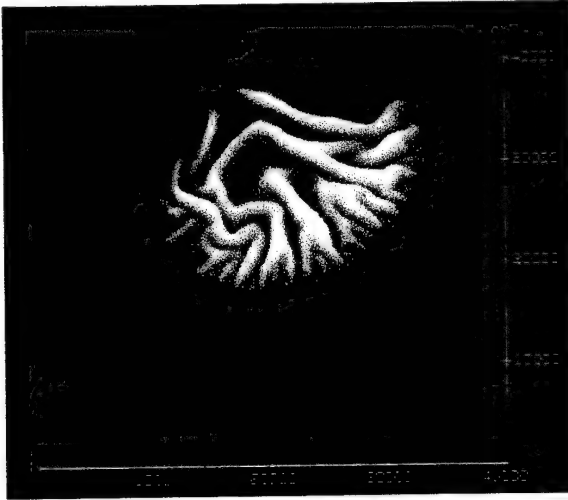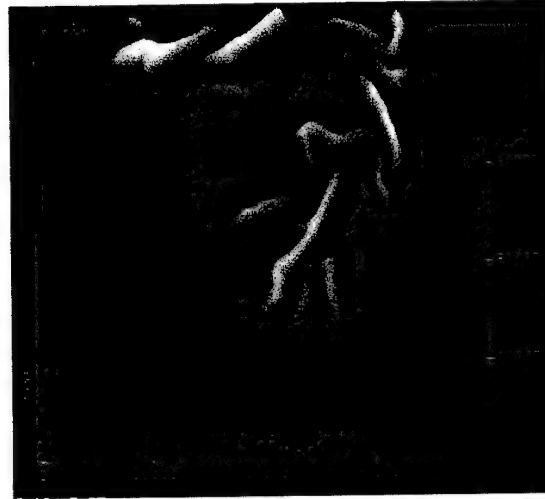
(d) S2 contamination after 25h of VUV

Figure 4. AFM images (40×40 μm scan) of a contaminated Ge sample before (a) and after exposure to different fluences of VUV: 6 h (600 ESH) (b), 12 h (1200 ESH) (c), and 25 h (2500 ESH) (d).

AFM measurements of the unexposed sample (Figure 4(a)) show a rather uniform distribution of ~10 μm size droplets. AFM images of VUV modified droplets (Figure 4 (b) – (d)) revealed a specific brain-like texture of these droplets together with an increasing size during irradiation. The maximum height difference ($Z_{max} - Z_{min}$) within a given area (40×40 μm scan) was as large as 2000-3000 nm after exposure to 12 h and 25 h of VUV, compared to height variations of about 500 nm before VUV exposure. The surface RMS roughness (defined as $R_q = [\Sigma(Z_i - Z_{ave})^2/N]^{1/2}$, where N is the number of data points; Z_i is the height at

point i; and Z_{ave} is the arithmetic mean of all the height values within the given area) was 44 nm for the unexposed sample and increased to about 300 nm after 12 and 25h of VUV exposure.

3.4. Surface analysis by XPS

The chemical composition of the outgassing products collected on Ge substrates and the chemical changes induced by VUV irradiation were studied by XPS. Figure 5 shows representative XP spectra in a wide binding energy range of pristine Ge substrate and a sample contaminated with outgassing products emitted at 125°C (high-temperature fraction only). About 15-20 at.% of surface carbon contamination and about 10-15 at. % of oxygen contamination were detected on different pristine Ge substrates after solvent cleaning. No Si contamination was detected prior to S2 black paint outgassing. The deposition of condensable volatile products resulted in the appearance of Si2p and Si2s core level lines at about 100 and 153 eV binding energy (BE), respectively. In addition, the intensity of C1s and O1s core level lines increased significantly, concurrently with a decrease of Ge3d core level line intensity.
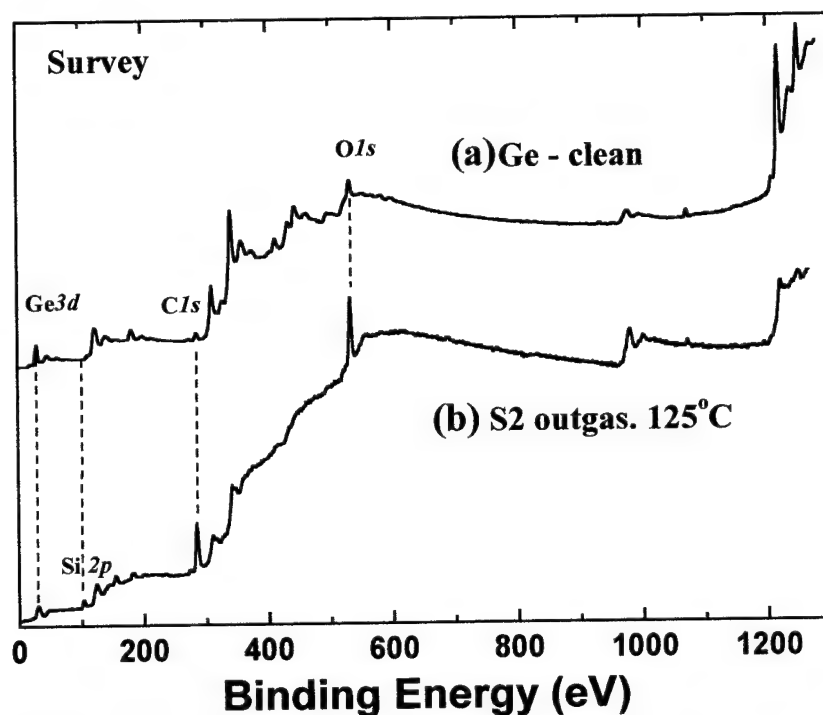

Figure 5. XP spectra in the 0-1250 eV binding energy range of a pristine Ge substrate (a) and a sample contaminated with outgassing products emitted at 125°C (b).

XPS data provide details about local bonding between C, Si, O, and Ge atoms due to chemical shifts of core level lines as a function of a charge transfer or oxidation state. The binding energy of the C$1s$ core level line changes from 285.0±0.5 eV for carbon atoms with low partial charge transfer in covalent-type chemical bonds (δ+) (like -C-H, -C-C-, or -C-Si) to 287.0±0.5 eV for more polar bonds, $C^{\delta++}$ (like -C-O-) and 289.5±0.5 eV for bonding states with higher charge transfer, $C^{\delta+++}$ (like -C=O) [8-9]. The position of Si$2p$ core level line is extremely sensitive to its oxidation state and varies from BE ~ 99 eV for elemental silicon (Si^0) to ~ 103-104 eV for SiO$_2$ (Si^{+4}) [8-10]. Similarly, the position of Ge$3d$ core level line varies from 29.4 eV for elemental Ge (or Ge$_x$Si$_y$ states) to ~ 33.0 eV for GeO$_2$ [9, 11]. The Ge$3d$ peak positioned at 31.8±0.3 eV is an evidence of GeO-type species formation [11]. The interpretation of O1s peak position is more ambiguous in most cases. Moreover, the position of O1s core level line at BE ~ 532-533 eV coincides with a Ge(L$_3$M$_{23}$M$_{23}$) Auger transition. This overlapping might give rise to uncertain calculation of oxygen atomic concentration [12].

The relative contribution of different bonding states and elemental composition of the contamination samples produced under different outgassing conditions was estimated from high-resolution core level lines using a standard curve synthesis procedure [13]. The results are summarized in Table 2.

Table 2. The surface elemental composition of Ge samples contaminated by S2 black paint under different outgassing conditions

Sample description BE, ±0.2eV Peak assignment	Ge		C			Si	O
	29.6	33.2	285.2	286.9	289.3	102.9	232.8
	Ge, Ge$_x$Si$_y$	GeO$_2$	C^0-$C^{\delta+}$ *	$C^{\delta++}$	$C^{\delta+++}$	PDMS	All
Ge, solvent clean	40.9	7.2	21.1	0	6.6	0	24.2
Ge/S2 75°C - fraction	4.7	17.9	18.1	4.3	2.2	2.6	50.2
Ge/S2, 100°C - fraction	1.9	13.7	35.6	2.2	0	8.2	38.4
Ge/S2, 125°C - fraction	7.9	5.1	51.8	0	0	10.7	24.5
Ge/S2 - all fractions (ASTM E 595 outgassing)	1.3	6	51.2	2.5	0	12.8	26.2

* Symbol δ refers to a partial charge transfer in covalent-type chemical bonds

The samples prepared under different outgassing conditions differ in (i) relative population of Ge^0 and GeO_2 bonding states; (ii) relative concentration of Si and (iii) the presence of -C-O- states. The possible interpretation of these results will be presented below.

The sample contaminated with outgassing products emitted at 125°C (high-temperature fraction only) was exposed to different fluences of VUV irradiation. After 6 h of VUV irradiation (600 ESH) the sample was exposed to ambient air for 24 h and then placed back into UHV system. The changes in chemical composition of the VUV modified surface before and after air exposure were monitored. The VUV exposure was continued for additional 6 h (total 1200 ESH) and then 13 h (total 2500 ESH) after one more interruption for 24 h of air exposure. The surface elemental composition was assessed from high-resolution XPS core level lines following each stage of VUV and air exposure. The results are summarized in Table 3. Figure 6 and Figure 7 show Ge*3d* and C*1s* XP spectra of a contaminated sample before and after exposure to VUV for 6 h (600 ESH) and the changes following an exposure of the VUV irradiated sample to air for 24 h, respectively.

Table 3. The surface elemental composition of Ge samples contaminated by S2 black paint outgassing products emitted at 125°C before and after exposure to different VUV irradiation doses as well as after exposure to ambient air

Sample description / BE, ±0.2eV / Peak assignment	Ge			C			Si		O
	29.6	31.6	33.2	285.2	286.9	289.3	102.9	103.9	232.8
	Ge, Ge_xSi_y	GeO	GeO_2	C^0-$C^{\delta+}$ *	$C^{\delta++}$	$C^{\delta+++}$	PDMS	SiO_2	All
Ge/S2 (125°C- fraction)	7.9	0	5.1	51.8	0	0	10.7	0	24.5
6h VUV (600 ESH)	8.4	1.7	3.2	42.7	7.6	0	6.4	5	23.5
24h air exposure	6.9	1.2	3.6	33.7	10.9	4.8	5.4	4.3	29.7
12h VUV (1200 ESH)	7.3	1.6	3	39.9	10.2	0	5.7	4.8	27.5
24h air exposure	5.8	0.9	2.7	33	12.3	2.1	4.7	3.9	31.6
25h VUV (2500 ESH)	6	1.3	2.7	42.8	8.1	2	5.1	5.1	26.9

* Symbol δ refers to a partial charge transfer in covalent-type chemical bonds
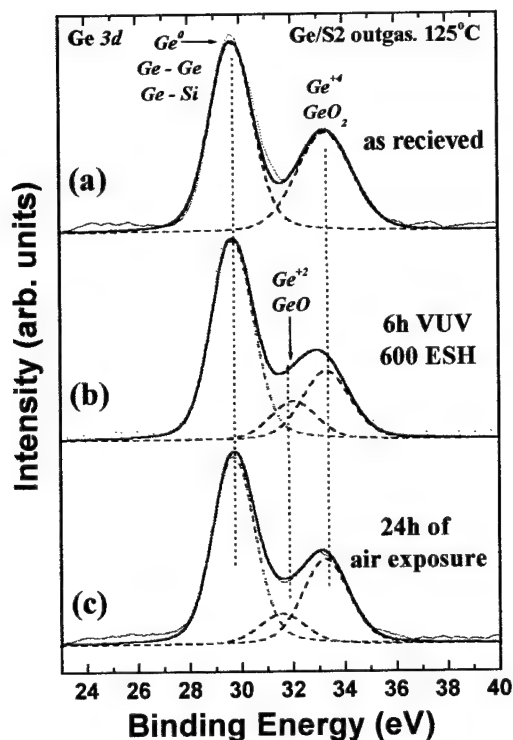
Figure 6. Ge*3d* XP spectra of contaminated sample before (a) after exposure to 6h VUV (b), and after exposure to ambient air for 24 h (c).
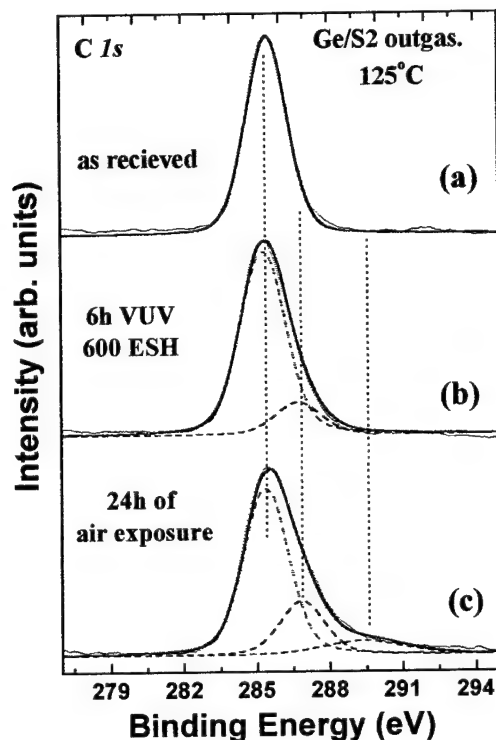

Figure 7. C*1s* XP spectra of contaminated sample before (a) after exposure to 6h VUV (b), and after exposure to ambient air for 24 h (c).

The following conclusions can be drawn from the observed results.

1. VUV exposure caused a redistribution of Ge oxidation states. Partial Ge reduction was observed which was accompanied by the appearance of intermediate Ge oxidation state associated with GeO. The relative population of this state reached about 13 at .% (of total Ge concentration in the analyzed region) after VUV exposure and decreased to about 10 at.% after 24h of air exposure.

2. Partial oxidation of Si was detected following VUV exposure through observation of a distinct SiO_2 state at BE ~ 104 eV. The relative population of this state was about 50 at.% after exposure to a maximum VUV fluence of 2500 ESH. Note that partial GeO_2 reduction concurrently with partial SiO_2 formation is consistent with the fact that Ge is generally accepted to be more electronegative than Si, so oxygen moves to silicon sites to form more stable SiO_2 [11, 12].

3. Significant broadening and apparent shift of C*1s* core level line-shape towards high binding energy were observed after VUV exposure and after air exposure, indicating the appearance of -C-O- states at about 286.9 eV. The relative population of this state attains

about 15at.% (of total carbon surface concentration) after VUV exposure and increases to about 22-24at.% after air exposure.

4. The exposure to air of the irradiated sample resulted in a modification of the XPS spectrum. The C$1s$ line shape modifications included an increase of the relative integral intensity of the 286.9 eV component and the appearance of a shoulder at 289.5 eV, very likely due to –C=O. These changes were associated with the increase of the oxygen concentration (Table 3).

4. Discussion

According to the submitted proposal and detailed experimental plan [1], the present work was supposed to address the following issues: (i) deposition of siliconic contaminants at different temperatures, (ii) the study of fundamental processes involved in the interactions of siliconic contamination with Vacuum and Near UV irradiation, and (iii) assessment of the influence of air exposure on the irradiated materials, comparing the results of *in-situ* and *ex-situ* XPS characterization of the specimens. Due to the technical problems and the time limitations we concentrated on the deposition and characterization of the outgassing products and VUV exposure of the selected samples, as well as the air exposure of the irradiated samples. However, some unexpected results and interesting directions for further studies were found in the present work. Note that due to the temporary failure of the XPS equipment, the outgassing products collected on Ge substrates were subjected to a relatively long air exposure. The consequences of this unplanned exposure will be discussed below.

4.1. The outgassing products

The present work studied the outgassing of S2 black siliconic paint and the effect of VUV irradiation on the deposited contamination. The outgassing products were characterized by FTIR spectroscopy as consisting predominantly of poly(dimethyl)siloxane (PDMS, $[(CH_3)_2SiO]_n$). However, different additives in the siliconic paint may have contributed to the collected outgassing products or may have affected a Ge sample used as a substrate. These additives included Methyltrimethoxysilane (which possibly gave rise to Si-O-C vibrations in the FTIR spectrum), Ethoxyethyl Ecetate 2 and aromatic solvents (Tolyene, O-Xylene and Ethylbenzene) [14]. Moreover, S2 paint exposed to high temperatures could release decomposition products such as carbon monoxide, carbon dioxide, and nitrogen oxide [14].

These substances also could affect the collected volatile products and react with the substrate surface.

The outgassing process was studied under different conditions: (i) standard outgassing procedure according to ASTM E 595 (125°C for 24 hr) and (ii) stepwise outgassing at three different temperatures (75°C, 100°C and 125°C). Only the sample deposited at 125°C (after evaporation of low-temperature fractions at 75°C and 100°C) was chosen for *in situ* VUV irradiation. This sample differed from a chemical point of view from all the other contaminated samples (see Table 2). According to a high-resolution Ge*3d* XP line shape, ~60 at.% of the detected Ge in this sample was present in a non-oxidized state, compared to ~20 at.% or less in all the other samples. According to the XPS peak position, this state may be assigned to Ge-Ge or Ge-Si bonds. The detection of a pure Ge is unlikely in this case since the total amount of outgassing products is relatively high. However, non-uniform and non-continuous surface coverage complicates the interpretation of the XPS results. It may be suggested that the low-temperature fractions of the outgassing products included oxygen-containing organic compounds which caused oxidation of Ge surface. Only when the low-temperature fraction was removed and the 125°C – fraction was collected, the oxidizing components did not contribute to the substrate-contamination interaction. In this case, the deposited PDMS could react with the clean Ge surface, giving rise to non-stoicheometric Ge_xSi_y bonding states.

Note that in all studied samples a significant amount of Ge was detected by XPS. The total Ge concentration was maximum for the sample containing the 75°C – outgassing fraction (~23 at.%) and it decreased to ~ 16 at.% and ~13 at.% for the samples containing the 100°C – and the 125°C – fractions, respectively. Minimum Ge concentration (~7 at.%) was detected for the sample which collected all the outgassing fractions during a standard outgassing procedure according to ASTM E 595. The sampling depth of the XPS for Ge and Si is similar and equal to about 50 Å. Thus, the detection of Ge by XPS in the contaminated samples may be attributed to: (i) very thin continuous contamination layer (less then 50 Å) and/or (ii) non-continuous and non-uniform type of contamination. The QCM measurements indicate that the average thickness of the contamination layer was about 500 Å or more for the 100°C and 125°C-fractions, assuming a continuous and uniform deposition (Chapter 3.1). However, this value was reduced significantly due to re-evaporation of the outgassing products, both in vacuum (as it was monitored by the QCM) and in air, during the samples unplanned storage (as was demonstrated by a decrease of the FTIR bands intensity of the spectrum after long storage of the contaminated samples in air). On the other hand, optical microscope

observations clearly showed a non-uniform type of contamination only for the samples containing the 125°C – outgassing fraction.

The contamination layer could grow in one of the three main deposition known modes: (i) three-dimensional island growth, (ii) two-dimensional layer-by-layer growth, and (iii) layer-plus-island growth [15]. Based on the above considerations, it may be suggested that the different outgassing fractions may be involved in different deposition modes. The question which of these modes was dominant for a particular outgassing fraction should be further studied. However, it should be noted that in all cases the deposition of a contamination layer included the following basic steps: (i) evaporation, (ii) mass transport, (iii) adsorption on the substrate surface, (iv) surface diffusion/migration, (v) surface reactions and incorporation of the condensable constituents into the contamination film.

4.2. Contamination modification by VUV

4.2.1. Morphology of the deposited contamination layer

The deposited contamination consisted of well-defined droplets. This can occur in the case of solvents or liquids evaporation or nucleation of outgassing products onto relatively cold (with respect to the contamination source) surfaces. It should be noted, however, that the formation of droplets is surprising in the case siliconic fluids. These fluids have very low surface tension (typically 20-25 dyn/cm for linear PDMS and increasing slightly with the degree of polymerization), permitting them to spread readily on most glass, metal and ceramic surfaces [16]. However, it may be suggested that microscopic scratches presented on the Ge substrate may have served as a preferential nucleation sites for contamination droplets formation.

The formation of visibly clean regions (free of contamination droplets) in the vicinity of large modified particles which was observed after VUV exposure may be considered as an evidence of surface migration (or diffusion) of small contamination droplets with subsequent agglomeration into larger aggregates. These large aggregates underwent VUV induced modifications, which resulted in the formation of a specific brain-like texture. It may be suggested that these structural transformations and texture formation were due to volatilization of low-molecular weight products and a cross-linking of the remaining polymeric matrix. As a result, large droplets exhibited surface contraction and wrinkled morphology. This situation may be imagined as solvent evaporation from a gel-like system.

This mechanism is consistent with previously published data on dimethyl silicones [17-18]. These materials are known to undergo cross-linking when subjected to gamma ray or

electron irradiation. Small radiation doses first increase the viscosity of the fluids due to formation of branched molecules, while at higher radiation doses the fluid eventually gels. These phenomena may take place also in the case of VUV irradiation, characterized by energy loss processes including ionization, bond breaking and local excitations. The modification of polymers by these processes may advance through scissioning and creation of volatile fragments (resulting in mass loss), as well as through cross-linking (resulting in a stable matrix formation without mass losses) leading to the formation of the observed brain-like features.

4.2.2. Contamination fixation by VUV

It was mentioned previously that during the VUV exposure, the sample temperature and residual pressure in the chamber increased to ~50°C and 1×10^{-8} Torr, respectively, after 12 h of continuous VUV exposure. The increase of the residual pressure may indicate the outgassing of sample holder and VUV source accessories, VUV induced evaporation of volatile fragments, as well as thermal evaporation of the deposited contamination.

In order to separate the influence of VUV exposure and thermal evaporation in vacuum, we carried out the following reference experiment. A Ge substrate contaminated by standard outgassing (according to ASTM E 595) of S2 black paint was placed into the UHV system and heated to 50°C for 18 h. The sample was analyzed by XPS before and after the thermal treatment. No changes in Ge$3d$, Si$2p$, C$1s$ or O$1s$ core level line-shapes and positions were found. However, a slight decrease of Si/Ge ratio (from 1.6 to 1.3) indicated a relative decrease of siliconic outgassing products in the analyzed region. This is consistent with the re-evaporation of the outgassing products studied by QCM. Re-evaporation kinetics studied by heating of the gold-coated QCM sensor indicated that nearly 95% of the outgassing products may evaporate by heating of the contaminated surface to 50°C in vacuum. It may be suggested that no chemical interaction between outgassing products and contaminated surface takes place in this case. On the other hand, samples exposed to VUV radiation, did not show significant changes in the Si/Ge ratio in the analyzed region before and after VUV exposure. Moreover, Si/Ge ratio even increased slightly from 0.82 to 1.02 after 25h of total VUV exposure. This may be an indication of VUV induced fixation of the contamination products.

Thus VUV induced modifications of siliconic contamination deposited on Ge substrates may include the following mechanisms:

(i)   surface diffusion/migration of small droplets forming larger aggregates;

(ii)   partial evaporation of low-molecular weight fragments;

(iii) substrate – contamination interaction resulting in partial GeO_2 reduction, formation of SiO_2, $\mathord{>}Ge\text{–}O\text{–}Si\mathord{<}$, and $\mathord{>}Ge\text{–}Si\mathord{<}$ fragments;

(iv) Si–C bond breaking with subsequent cross-linking between –Si–O–Si–O– backbones;

(v) Si–O bond breaking and partial scissioning of polymeric chain;

(vi) C–H bonds breaking;

This demonstrates that the interaction of silicone-based contamination products with Vacuum UV irradiation is rather complicated and include also contamination – substrate interactions. This system should be further studied in order to clarify the predominant reaction route and factors affecting it.

4.3. Air exposure of the deposited outgassing products and VUV irradiated samples

As was mentioned above, due to the technical problem, the outgassing products collected on Ge substrates were subjected to a relatively long exposure to ambient air (3 months). This may have affected the samples. Indeed, partial evaporation of the deposited samples in air was reflected by an increase of the transmission intensity of FTIR spectrum after long storage of the contaminated samples in air. Moreover, the changes in the FTIR spectrum of indicated some intra-molecular transformations in air. This shows the necessity to develop a system for *in-situ* outgassing products deposition, in addition to *in-situ* irradiation and characterization. Indeed, we plan to incorporate in our space simulation and characterization facility in the near future an additional high vacuum chamber with effusion cell for *in-situ* contamination deposition.

Another issue is the need and importance of *in-situ* studies of the interaction of outgassing products with the simulated space environment. According to our knowledge, the surface analyses of all the materials exposed in space experiments were performed *ex-situ*; i.e. the exposed samples reacted with the ambient atmosphere for at least 24 hours and probably much more before analyzing them. The unique feature of the present work was the use of the *in-situ* diagnostic probes to measure the VUV irradiation effects on materials, without exposure to the ambient environment that could react with the degraded surfaces and alter their chemical composition. Our data clearly demonstrates that contaminated surfaces that were VUV irradiated, reacted with air, increasing the oxygen content and chemically reacting with carbon creating -C-O- and -C=O bonds. Thus, *in-situ* characterization of the modified surfaces is required for the elucidation of the fundamental processes involved in the interaction of materials with the simulated space environment.

4.4. Open questions and suggested directions for further studies.

The present work led to new questions and directions for further studies. Some of them are listed below.

The exact mechanism of droplet formation during the outgassing of silicone-based materials should be further studied. The substrate temperature and outgassing rate, as well as surface roughness and type may determine the type of contamination layer formation. This may have important implications since a droplet-like structure of the contamination products may affect significantly the reflection/absorption properties of a contaminated surface. Moreover, a theoretical modeling of the contamination effects on optical properties should take into account the fact that the contamination layer is non-continuous and non-uniform in thickness.

The migration (or diffusion) of small contamination droplets and the VUV induced formation of large aggregates with specific brain-like texture were the most surprising results of the present work. The reproducibility and the mechanism of these phenomena should be further studied.

The interaction of siliconic contamination with different types of surfaces (like glass, MgF_2, Al, and others) should be studied from both chemical and morphological points of view. Contamination fixation and modification might be affected by surface properties.

In-situ contamination preparation, irradiation and characterization require further development and modification of the existing experimental facilities. This includes the possibility of simultaneous outgassing from contamination source together with the irradiation of the outgassed molecules.

The influence of irradiation intensity (acceleration factor) should be addressed in future studies.

5. Summary and Conclusions

As a result of this research we got an insight into some of the aspects involved in the formation of siliconic contaminants and their interactions with the space environment. These included the following issues:

a) The nature and morphology of outgassing products originating from silicone-based compounds depend on the outgassing conditions, namely the temperature of the material and the outgassing rate.

b) The outgassing products may interact chemically with the substrate material. Since this interaction might affect the nature of the contaminated surfaces it is very important to continue the study on different types of substrates.

c) The mechanism of the interactions of silicone-based contamination products with Vacuum UV irradiation is rather complicated. VUV exposure causes changes in the surface morphology of the deposited samples as well as intra- and inter-molecular rearrangements in the polymeric chains and chemical modification of the substrate-contamination interface. In addition, a combined QCM and XPS studies indicate partial fixation of the contamination layer under VUV irradiation.

d) The influence of air exposure on the irradiated contaminants was assessed. The results of our work strongly indicate the need and importance of *in situ* studies of the interactions between the outgassing products and the simulated space environment.

The present work raised new questions and suggested novel directions for further studies in the field of formation of contamination products and their interactions with the space environment.

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